Journal of Magnetism and Magnetic Materials 400 (2016) 295–299

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

$(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$: A copper-based bulk form diluted magnetic semiconductor with orthorhombic $BaCu_2S_2$-type structure

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ARTICLE INFO

Article history:
Received 20 June 2015
Accepted 5 July 2015
Available online 6 July 2015

Keywords:
$BaCu_2Se_2$
Diluted magnetic semiconductor
Curie temperature
Ferromagnetic ordering

ABSTRACT

A new copper-based bulk form diluted magnetic semiconductor (DMS) $(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$ (x=0.075, 0.10, 0.125, and 0.15) with T_C ~18 K has been synthesized. K substitution for Ba introduces hole-type carriers, while Mn substitution for Cu provides local spins. Different from previous reported DMSs, this material crystallizes into orthorhombic $BaCu_2S_2$-type crystal structure. No ferromagnetism is observed when only doping Mn, and clear ferromagnetic transition and hysteresis loop have been observed as K and Mn are codoped into the parent compound $BaCu_2Se_2$.

1. Introduction

Diluted magnetic semiconductors (DMSs) take advantage of spin and charge degrees of freedom, which has received extensive attentions ever since the ferromagnetism was observed in (Ga,Mn)As [1–5]. However, spin and charge doping simultaneously via Mn substitution for Ga prohibit the individual control of spin and charge density. On the other hand, because of the mismatch valences of Mn^{2+} and Ga^{3+} ions, high quality metastable (Ga,Mn)As only exists in thin film state which is fabricated by low temperature molecular beam epitaxy (LT-MBE). Thin film specimens preclude the utilization of some powerful probes such as nuclear magnetic resonance (NMR) and neutron scattering that are based on bulk form specimens to provide complementary information at a microscopic level. So far, the origin of ferromagnetism in DMSs has not been fully understood. To overcome these difficulties, exploring new bulk form DMSs with decoupled spin and carrier doping becomes necessary.

Through several years of efforts, many bulk form DMSs with spin and charge decoupled doping have been synthesized, which can be roughly classified into three classes according to their structure type. The first class belongs to the cubic structure, and consists of Li(Zn,Mn)As [6], Li(Zn,Cr)As [7] and Li(Zn,Mn)P [8], which is isostructural to (Ga,Mn)As. The second class has a tetragonal structure, and consists of (Ba,K)$(Zn,Mn)_2As_2$ [9], (La,Ba)(Zn,Mn)AsO [10] and (La,Ca)(Zn,Mn)SbO [11]. The third class has a hexagonal structure, and consists of (Sr,Na)$(Zn,Mn)_2As_2$ [12] and (Sr,K)$(Zn,Mn)_2As_2$ [13]. It is worth noting that the Curie temperature in (Ba,K)$(Zn,Mn)_2As_2$ system has reached ~ 230 K [14], which has exceeded the record of (Ga,Mn)As. Previous muon spin relaxation (μSR) measurements have demonstrated that bulk form DMSs share the same ferromagnetic mechanism with (Ga,Mn)As [15,16]. However, muon spin relaxation (μSR) measurements on (Sr,Na)$(Zn,Mn)_2As_2$ with hexagonal $CaAl_2Si_2$-type structure suggest different exchange interactions between Mn atoms [12]. The aforementioned DMSs are all zinc-based semiconductors. Recently, Yang et al. synthesized a copper-based bulk form DMS, (La,Sr)(Cu,Mn)SO, with T_C up to ~ 200 K [17].

$BaCu_2Se_2$ is a copper-based semiconductor with orthorhombic $BaCu_2S_2$-type crystal structure and a band gap of ~ 1.3 eV [18]. In this system, Ba atoms are located in the channels constructed by $CuSe_4$-tetrahedrons, shown in Fig. 1(b). In this paper, we report a new copper-based bulk form DMS $(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$. Ferromagnetic transition with Curie temperature T_C ~ 18 K and clear hysteresis loop is observed when K and Mn are codoped into the parent compound $BaCu_2Se_2$.

2. Experiments

Polycrystalline specimens of $(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$ were synthesized by solid state reaction from the original elements (99.9% or

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http://dx.doi.org/10.1016/j.jmmm.2015.07.005
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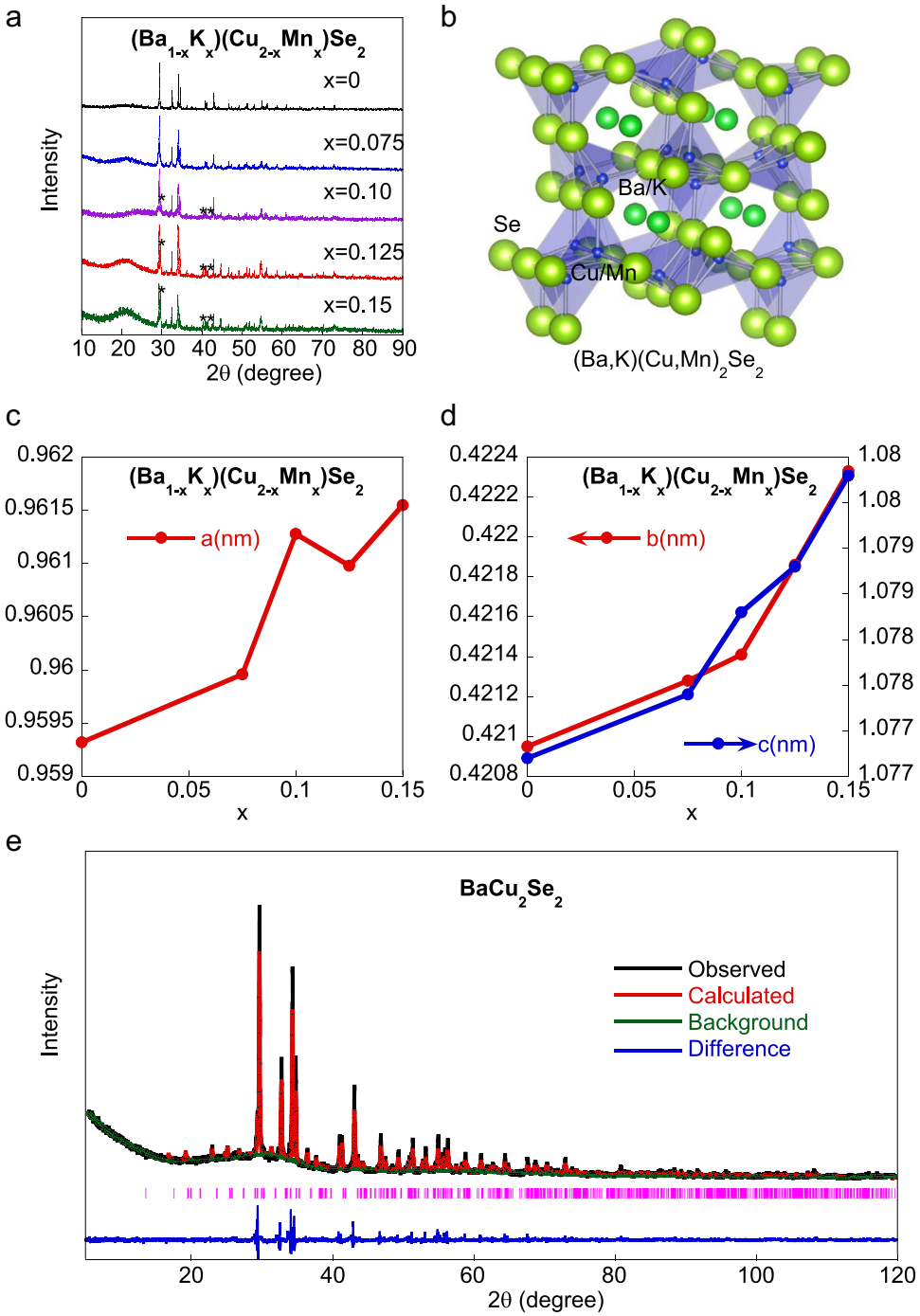

Fig. 1. (a) X-ray diffraction patterns for $(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$ with $x=0$, 0.075, 0.10, 0.125, and 0.15. Traces of non-magnetic impurity $CuSe_2$ with orthorhombic structure are marked by stars. (b) The crystal structure of $(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$ belonging to orthorhombic $BaCu_2S_2$-type structure. (c) and (d) Lattice constants of $(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$ for various doping concentrations. (e) Rietveld refinement of the powder X-ray diffraction for parent compound, $BaCu_2Se_2$.

higher purity), which is stored and handled in an argon filled glove box (the percentage of O_2 and H_2O < 0.1 ppm). Ba pieces, K lumps, Cu powders, Mn powders and Se shots were mixed according to the nominal composition of $(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$ and heated at 500 °C for 48 h in evacuated silica tubes. The products were then grounded, pelletized, and sealed in evacuated silica tubes, and annealed at 500 °C for another 83 h. Powder X-ray diffraction was performed at room temperature using a PANalytical X-ray diffractometer (Model EMPYREAN) with a monochromatic $CuK_{\alpha 1}$ radiation. The DC magnetization measurements were conducted on Quantum Design Magnetic Property Measurement System (MPMS-5). The electrical resistivity was measured on sintered pellets with typical four-probe method.

3. Results and discussion

In Fig. 1(a), we show the X-ray diffraction patterns for $(Ba_{1-x}K_x)(Cu_{2-x}Mn_x)Se_2$ with K and Mn of equal doping levels ($x=0$, 0.075, 0.10, 0.125, and 0.15). The Rietveld refinement for $BaCu_2Se_2$ with parameters $R_{wp}=8.6\%$, $R_p=6.2\%$ indicates that the system crystallizes into orthorhombic $BaCu_2S_2$-type structure (space group *Pnma*), as shown in Fig. 1. Traces of paramagnetic